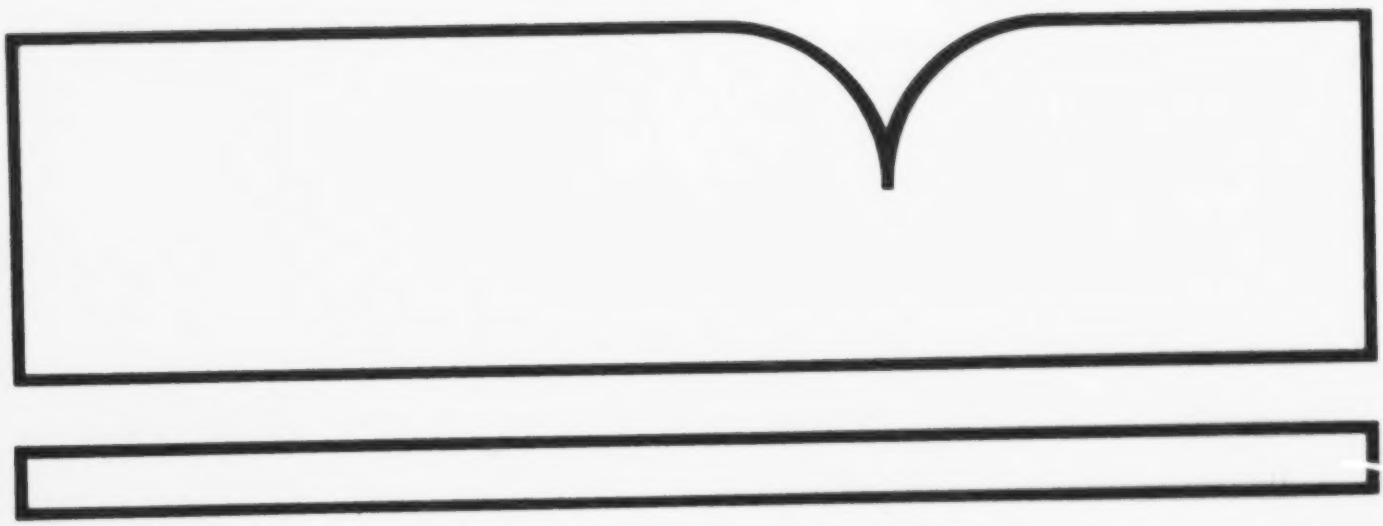
PB87-179990

Chemistry of Oxidant Formation Implications for Designing Effective Control Strategies

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Apr 87



U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-179990

EPA/600/D-87/114
April 1987

CHEMISTRY OF OXIDANT FORMATION

IMPLICATIONS FOR DESIGNING EFFECTIVE CONTROL STRATEGIES

by

Marcia C. Dodge

U. S. Environmental Protection Agency
Atmospheric Sciences Research Laboratory
Research Triangle Park, NC 27711

ATMOSPHERIC SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/D-87/114	2.
3. RECIPIENT'S ACCESSION NO. PB87 179990/AS	
4. TITLE AND SUBTITLE CHEMISTRY OF OXIDANT FORMATION: IMPLICATIONS FOR DESIGNING EFFECTIVE STRATEGIES	5. REPORT DATE April 1987
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Marcia C. Dodge	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Atmospheric Sciences Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	10. PROGRAM ELEMENT NO. A101/B/63/20/6077 (FY-87)
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

A simple moving box model was used to assess the effect of various control strategies on predictions of ozone formation in urban areas. It was found that the effectiveness of a proposed control measure depends critically on the ratio of the Volatile Organic Compounds (VOC) and NO_x precursors that are emitted into the urban environment. Depending on the assumptions made about the ratio of the VOC and NO_x emissions, a strategy involving simultaneous control of VOC and NO_x can be more or less effective in reducing downwind ozone levels than a strategy involving reduction of only VOC. In all cases, however, it was found that NO_x control, by itself, has a detrimental impact on ozone levels near source areas. Further, when NO_x control accompanies VOC control, ozone concentrations near source areas are higher than would occur if VOC alone is reduced. NO_x control, therefore, could result in greater population exposure to high ozone levels than would be the case if only VOC is reduced.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 25
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

CHEMISTRY OF OXIDANT FORMATION

IMPLICATIONS FOR DESIGNING EFFECTIVE CONTROL STRATEGIES

by

Marcia C. Dodge
U. S. Environmental Protection Agency
Atmospheric Sciences Research Laboratory
Research Triangle Park, NC 27711

ABSTRACT

A simple moving box model was used to assess the effect of various control strategies on predictions of ozone formation in urban areas. It was found that the effectiveness of a proposed control measure depends critically on the ratio of the Volatile Organic Compounds (VOC) and NO_x precursors that are emitted into the urban environment. Depending on the assumptions made about the ratio of the VOC and NO_x emissions, a strategy involving simultaneous control of VOC and NO_x can be more or less effective in reducing downwind ozone levels than a strategy involving reduction of only VOC. In all cases, however, it was found that NO_x control, by itself, has a detrimental impact on ozone levels near source areas. Further, when NO_x control accompanies VOC control, ozone concentrations near source areas are higher than would occur if VOC alone is reduced. NO_x control, therefore, could result in greater population exposure to high ozone levels than would be the case if only VOC is reduced.

INTRODUCTION

The control of Volatile Organic Compounds (VOC) has been the principal approach used in recent years to reduce ambient concentrations of ozone in urban areas. Several recent reviews on control strategies for ozone (CARB, 1986; Meyer, 1986), however, have suggested that there may be situations where control of NO_x emissions could also be beneficial in reducing urban ozone levels. The present study was undertaken in an effort to determine if NO_x control, either alone or in combination with VOC control, could be effective in reducing ozone levels in urban areas.

The effectiveness of any measure that might be adopted to limit ozone formation is largely determined by the ratio of the VOC and NO_x precursors that are emitted into the environment. The fact that this is the case is apparent if one understands the chemical processes that are responsible for the production of ozone. In the following section, a discussion of the chemistry of oxidant formation and the relationship between emission control measures and VOC/NO_x ratios is presented. The results of simulations conducted with a simple box model to investigate emission control strategies are also presented and the implication of these results on the possible benefits to be achieved through NO_x control is discussed.

CHEMISTRY OF OXIDANT FORMATION

Ozone formation in the atmosphere is governed by three reactions. Nitrogen dioxide photolyses in sunlight to produce nitric oxide and an oxygen atom:

$$NO_2 + h\nu \rightarrow NO + O \qquad (1)$$

The O atom liberated reacts rapidly with oxygen in the presence of a third body to generate ozone:

$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$

In the absence of any competing reactions, the ozone produced in Reaction (2) reacts with NO to regenerate NO_2:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3)$$

As a result of these three reactions, an equilibrium or steady-state condition is established and the concentration of ozone is given by the Steady-State Equation,

$$[O_3] = k_1 \times ([NO_2]/[NO]) \times \text{Constant},$$

where k_1 is the rate of photolysis of NO_2. Most of the NO_x emitted into the urban environment is in the form of NO. In fact, the ratio of NO_2-to-NO emissions from combustion sources is approximately 1-to-9 (U.S. EPA, 1982). Given such a low ratio, it is apparent from the Steady-State Equation that there will be little build-up of ozone in the atmosphere unless there is a mechanism for converting NO to NO_2. Reactions (1) - (3) do not provide such a mechanism since every time an O_3 molecule is formed, it is immediately consumed through reaction with NO. An alternate pathway is needed that will lead to the oxidation of NO without destroying O_3 in the process. Such a pathway is provided through the oxidation of VOC's.

VOC's participate in a number of reactions that increase the NO_2-to-NO ratio and consequently increase the levels of O_3 observed in the atmosphere. For example, aldehydes, which are components of auto exhaust, photodissociate in sunlight to produce HO_2 radicals that rapidly oxidize NO:

$$RCHO + h\nu \rightarrow HO_2 \quad (4)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (5)$$

The hydroxyl radicals liberated in this process react readily with most hydrocarbon species to produce alkylperoxy radicals which also oxidize NO:

$$OH + HC \rightarrow RO_2 \quad (6)$$

$$RO_2 + NO \rightarrow RO + NO_2 \quad (7)$$

The resulting RO radicals react readily with oxygen:

$$RO + O_2 \rightarrow RCHO + HO_2 \quad (8)$$

The aldehydes formed in this process can either photodissociate to start the process over again or they can react with OH radicals:

$$RCHO + OH \rightarrow RCO_3 \quad (9)$$

The acylperoxy radicals formed in this process can also oxidize NO:

$$RCO_3 + NO \rightarrow RO_2 + NO_2 \quad (10)$$

In addition to Reactions (4) - (10), which increase the NO_2/NO ratio and promote O_3 formation, there are also reactions that tend to decrease the NO_2/NO ratio and limit O_3 production. The two most important of these processes are the reactions of OH and RCO_3 radicals with NO_2 to form nitric acid and peroxyacetylnitrate, respectively:

$$OH + NO_2 \rightarrow HNO_3 \quad (11)$$

$$RCO_3 + NO_2 \rightarrow PAN \quad (12)$$

The significance of these reactions will become apparent later.

The rate of conversion of NO to NO_2 in the atmosphere is governed largely by the VOC-to-NO_x ratio. At low ratios (VOC/NO_x < 5:1), the system is VOC-limited and NO_x-rich. Few RO_2 radicals are produced as a result of hydrocarbon oxidation (Reaction 6) and the rate of conversion of NO to NO_2 is slow. The VOC's may be depleted before all of the NO has been oxidized to NO_2, in which case the build-up of ozone will be limited. An effective control strategy in such a situation would be to reduce the limiting reactant which is VOC. Such a strategy would have the effect of further decreasing the number of RO_2 radicals available to oxidize NO and ozone levels would decrease.

At high VOC/NO_x ratios (VOC/NO_x > 20:1), the system is VOC-rich and NO_x-limited. The radicals produced during oxidation of the VOC's are in excess of the number needed to oxidize NO. The excess radicals consume NO_2 through Reactions (11) and (12) and limit O_3 production. An effective control strategy in such a situation would be to reduce the limiting reactant which in this case is NO_x. Fewer of the excess radicals would then be consumed through reaction with NO. More of the radicals would be available to react with NO_2 to remove it from the system and retard O_3 formation.

At moderate VOC-to-NO_x ratios, both VOC and NO_x are present in the amounts needed to generate ozone effectively. The VOC's produce sufficient RO_2 radicals to oxidize all NO to NO_2. NO_x levels are also sufficient to generate high levels of NO_2. In such a situation, control of either VOC or NO_x should lead to reduced ozone levels.

The role of the VOC/NO_x ratio in determining the effectiveness of various control measures can be better illustrated through the use of an ozone isopleth diagram. Such a diagram is illustrated in Figure 1. In this diagram, maximum daily ozone concentrations are plotted as a function of early morning levels of NO_x and non-methane

hydrocarbons (NMHC).* These isopleths were generated with a very simple moving box model, which is the basis of the Empirical Kinetics Modeling Approach (EKMA) that is used to estimate the amount of precursor control needed to reduce peak hourly ozone levels (U.S. EPA, 1977). Regardless of the model used to generate the diagram, whether it is a simple box model or a sophisticated dispersion model, the shape of the diagram will be similar. All such diagrams show three distinct regions. In the upper left-hand corner of the diagram, the isopleth lines are parallel and have a positive slope. There is a region in the middle of the diagram where the isopleths exhibit considerable curvature and finally, in the lower right-hand corner, the isopleth lines are all parallel to the x-axis.

The isopleth diagram can be used to understand the relationship between emission control measures and VOC/NO_x ratios. Figure 1 demonstrates the effect of reducing ozone precursor concentrations by 25% in the low VOC/NO_x regime of the diagram where VOC's are the limiting reactant in the O_3-formation process. Point A corresponds to a VOC/NO_x ratio of 3:1 and a maximum ozone concentration of 0.24 ppm. Reducing VOC concentrations by 25% will decrease peak ozone to 0.12 ppm (Point B). Since the curves have a positive slope, however, a 25% decrease in NO_x will lead to an increase in ozone concentration as can be seen by Point C which corresponds to an ozone level of 0.29 ppm. To achieve the same benefit that is obtained through a 25% reduction in VOC, NO_x concentrations would have to be reduced by 95% (Point D).

Figure 2 demonstrates the effect of reducing ozone precursors in the high VOC/NO_x regime of the diagram where VOC's are in excess of the amount needed to generate O_3 effectively. Starting at Point A, which corresponds to a VOC/NO_x ratio of 30:1, a 25% reduction in NO_x

*In this paper, VOC and NMHC will be used interchangeably. Usually, however, NMHC is used to denote ambient concentrations while VOC is used to denote emissions of organic compounds.

will decrease ozone levels by approximately 15% (Point B). Because the ozone isopleths are parallel to the x-axis, however, a 25% reduction in VOC will cause no change in predicted ozone levels (Point C). To achieve the same benefit in O_3 that is achieved through a 25% reduction in NO_x, VOC levels would have to be reduced by 70% (Point D.)

The effect of reducing O_3 precursors at intermediate ratios is shown in Figure 3. It is in this region of the diagram where control of either VOC or NO_x should lead to reduced O_3 levels. In general, this region encompasses VOC/NO_x ratios between about 5:1 and 20:1. Most urban areas fall within this region. In a recent analysis of VOC and NO_x measurements conducted in 29 cities, it was found that 25 of the cities had median VOC/NO_x ratios that fell between 8 and 15 with an overall median value of about 12:1 (Baugues, 1986). Starting at Point A in Figure 3, which corresponds to a VOC/NO_x ratio of 12:1, it can be seen that a 25% reduction in either VOC or NO_x concentrations is equally effective. Control of either will reduce ozone from 0.28 to 0.25 ppm. If both VOC and NO_x are controlled by 25% (Point D), peak ozone concentrations would be reduced even further to about 0.23 ppm.

Judging from the example shown in Figure 3, it appears that control of either VOC or NO_x might be equally effective and control of both precursors might be the most effective strategy of all for urban areas having typical VOC/NO_x ratios. In the example shown in Figure 3, however, the control measures implemented were not sufficient to reduce O_3 to the U. S. National Ambient Air Quality Standard of 0.12 ppm. The amount of reduction that would be needed to achieve the O_3 standard for this particular case is shown in Figure 4. As is evident from this figure, the most effective strategy for achieving the O_3 standard would be to control VOC. The majority of the modeling studies conducted to date do suggest that a pure VOC control strategy is the most effective one for achieving the ozone standard. Many of these studies, however, suggest that some other type of control strategy might be more

effective in the short term for achieving more immediate benefits. Figure 5 presents the results of one such study that was conducted by Meyer (1986). Meyer first constructed an isopleth diagram using certain assumptions regarding the reactivity of the urban VOC mix, emission patterns, dilution, etc. The isopleth diagram was then used to look at the effect of various control scenarios on daily maximum O_3 levels. In this example, the VOC/NO_x ratio and the daily maximum ozone were assumed to be 12:1 and 0.24 ppm, respectively. Figure 5 shows the decrease in ozone that would be achieved through control strategies involving relative reductions in VOC, NO_x or both VOC and NO_x. It is evident from this figure that, for moderate reductions in ozone precursors, the least effective strategy would be control of VOC alone. For example, a 30% reduction in NO_x would be more effective than a 30% reduction in VOC and the most effective strategy would be to control both by 30%. The curves, however, eventually cross and the most effective strategy for achieving the ozone standard would be to control only VOC.

The results presented in Figures 3 and 5 suggest that, if we are looking for early reductions in ozone and maximum short-term benefits, the most effective strategy might be to adopt a control measure that involves reduction of both VOC and NO_x. These figures, however, only demonstrate the potential benefit of emission reductions on the daily maximum ozone level, regardless of where that maximum occurs. The figures do not indicate how ozone levels throughout an urban area might be impacted by emission reductions. In order to investigate the effect of VOC and/or NO_x reductions on area-wide ozone levels, a series of simulations were carried out using a simple model. The results of these simulations are presented in the following sections.

SIMULATION CONDITIONS

A simple one-cell moving box model was used to assess the effect of VOC and NO_x control strategies. For the baseline condition, the VOC and NO_x concentrations in the box at the start of the simulation were assumed to be 1.0 ppmC and 0.1 ppm, respectively, for an initial VOC/NO_x ratio of 10:1. The initial concentration of NO_2 was assumed to be 25% of the initial NO_x. Simulations were carried out from 0800 to 1800 hours using a solar radiation profile that corresponded to summer solstice at 34° latitude. Emissions were added to the box as it moved along its trajectory. It was assumed that the VOC/NO_x ratio of the added emissions was also 10:1, the same as the ratio of the initial mix. Emissions equivalent to 70% of the initial VOC and NO_x concentrations were added over an 8-hour period, with the largest fraction of the added emissions occurring during the first several hours of the simulation. The mixing height was allowed to vary from 250 m to 1235 m. As the mixing height rose, ozone and aged VOC's from aloft were entrained into the box. The concentrations of the entrained ozone and VOC pollutants were 0.05 ppm and 0.025 ppmC, respectively. The composition of the surface-layer VOC's was based on a recent analysis of VOC measurements that were conducted between 0600 and 0900 hours in 22 cities over a two-year period (Baugues, 1986). The composition of the VOC's entrained from aloft was based on an analysis of aircraft VOC measurements that were conducted over four different cities (Baugues, 1987). The chemical mechanism used in the simulations was the Carbon-Bond IV Mechanism that was recently developed by Whitten and Gery (1986). The CBM-IV contains 70 reactions and 28 species; VOC's are partitioned among seven organic classes. The mechanism has been extensively tested against smog chamber data collected in several different chamber facilities.

Simulations were conducted using a computer program developed by Jeffries (1987). The program is designed to run on an IBM PC/XT/AT

or fully compatible computer. The software package contains many of the same options that are available in the OZIPM-2 computer program (Gipson, 1984a) that is designed for use on mainframe computer systems.

SIMULATION RESULTS

The O_3 profile generated for the baseline condition ($[VOC]_i$ = 1.0 ppmC, $[NO_x]_i$ = 0.1 ppm) is shown in Figure 6. Also shown is the effect of reducing the initial VOC concentration and the added VOC emissions by 50%. The x-axis in this figure can be viewed as distance downwind from the source area as well as time. What is evident from the profiles shown in this figure is that VOC control leads to reduced ozone levels at all points along the trajectory. As a consequence, ozone levels throughout the urban area as well as downwind ozone levels are expected to be lowered if a VOC control strategy is adopted. This is not the case, however, if the initial NO_x and the NO_x emissions are decreased by 50%. As shown in Figure 6, reduction in NO_x leads to an increase in ozone levels in the early stages of the simulation when source emissions are greatest. Since more people tend to live in the center of urban areas than in downwind locations, NO_x control could result in increased population exposure to ozone.

A comparison of the NO_x and VOC control profiles shown in Figure 6 indicates that, along most of the trajectory, ozone levels following NO_x control are considerably higher than O_3 levels following VOC control, in some cases by as much as a factor of three. The curves, however, do come together in the late stages of the simulation, and the maximum ozone level obtained following NO_x control is comparable to the maximum ozone obtained following VOC control (0.185 vs. 0.190 ppm).

The effect of reducing both VOC and NO_x by 50% is shown in Figure 7. During the first half of the simulation, ozone levels are

higher when both precursors are controlled than when only VOC is controlled. Downwind ozone levels, however, are substantially lower for the case where both VOC and NO_x are controlled (0.16 vs. 0.19 ppm). Combined VOC and NO_x control, therefore, does reduce peak ozone; consequently, downwind ozone levels should be reduced if such a control strategy were adopted.

Judging from the results presented in Figure 7, it appears that a strategy involving simultaneous control of VOC and NO_x might be more effective than a strategy involving reduction of only VOC. There is one important point that should be noted, however. The simulations presented in Figures 6 and 7 were conducted assuming that the VOC/NO_x ratio of the emissions was the same as the ratio of the pollutants present in the box at the start of the simulations. For the baseline simulation, this led to a VOC/NO_x emission ratio of 10:1. This ratio was selected because urban VOC and NO_x measurements indicate that the ambient ratio is at least as high as 10:1 in most urban areas (Baugues, 1986). Existing emission inventories, however, suggest that ambient VOC/NO_x ratios should be considerably lower than 10:1. Recent reviews of emission inventories indicate that there may be a factor of two discrepancy between VOC/NO_x ratios based on emission inventories and those derived from ambient measurements (Ching et al., 1986, Westberg and Lamb, 1985). To judge the effect of this uncertainty in emission estimates, the simulations presented in Figures 6 and 7 were repeated using an emissions profile derived from an analysis of the St. Louis RAPS emission inventory (Gipson, 1984b). This profile resulted in a VOC/NO_x emission ratio of 5:1 in contrast to the 10:1 ratio that was used for the baseline simulation shown in Figures 6 and 7.

The results obtained when the ratio of the VOC/NO_x emissions was reduced to 5:1 are shown in Figures 8 and 9. As in the earlier set of simulations, the VOC/NO_x ratio of the initial mix was still assumed to be 10:1 for the baseline simulation; only the ratio of the added

emissions was changed. A comparison of the effect of NO_x control vs. VOC control is shown in Figure 8. If this figure is compared with Figure 6, it is apparent that the increase in ozone that occurs during the early stages of the simulation when NO_x is reduced is more pronounced when the ratio of VOC/NO_x emissions is 5:1 than when it was 10:1. In addition, although the previous set of simulations showed peak downwind ozone levels that were comparable when either NO_x or VOC was reduced, the simulations presented in Figure 8 show that VOC control is clearly more effective than NO_x control in reducing peak ozone as well as ozone all along the trajectory. The maximum O_3 concentration after VOC control is 0.15 ppm in contrast to the 0.22 ppm that is obtained following NO_x control.

The ozone profile generated when both VOC and NO_x are reduced by 50% is shown in Figure 9 for the case with the lower VOC/NO_x emission ratio. If this profile is contrasted with the profile obtained when only VOC is reduced, it is apparent that control of NO_x in addition to VOC is counterproductive. This is in contrast to the results presented in Figure 7 which suggested that a combination of VOC and NO_x controls would be the most effective strategy for reducing downwind levels of ozone.

DISCUSSION

The ozone profiles presented in Figures 7 and 9 suggest that control of both VOC and NO_x could be more or less effective than control of VOC alone depending on the assumptions made regarding the ratio of the precursors that participate in the ozone-forming process. Comparable results have been obtained in modeling studies that have been conducted with sophisticated photochemical grid models. In a study sponsored by the California Air Resources Board (SCAQMD, 1981), the urban airshed model developed by Systems Applications, Inc. was used to investigate the effect of emission reductions in the South

Coast Air Basin. In that study, the model was exercised for a one-day period beginning at 0500 hours. The model was initialized using surface air monitoring data for VOC and NO_x. Initial concentrations in the aloft layers were assumed to be equal to the concentrations in the ground-level cells of the model. As a consequence of using ambient data to initialize the model, the initial concentrations of VOC and the resulting VOC/NO_x ratios were high in comparison to the values that would be derived from the emission inventory. The simulations, therefore, were driven by the initial conditions and not by the emission inventory.

Using the scenario described above, the model developers looked at the effect of reducing either VOC or both VOC and NO_x by 50%. They found that VOC control alone was less effective in reducing the daily maximum O_3 concentration than control of both VOC and NO_x. A 50% reduction in VOC led to a 19% decrease in the area-wide predicted ozone maximum whereas a 50% decrease in both VOC and NO_x reduced the basinwide predicted maximum by 26%. They found, however, that ozone concentrations near the source areas were higher when both VOC and NO_x were reduced than when only VOC was reduced. These results are in qualitative agreement with the results presented in Figure 7.

In a subsequent study (Tesche et al., 1984), the model developers again exercised their urban airshed model to look at the effect of emission reductions in the South Coast Air Basin. In this later study, however, the model was exercised for a two-day period so that the results on the second day would be governed primarily by the emissions and not by the air quality data used to initialize the simulation. Thus, in contrast to the earlier work, the simulations conducted in this later study were driven by the low VOC/NO_x ratio of the emission inventory as opposed to the much higher VOC/NO_x ratio of the ambient measurements. In this study, as in the previous one, the model developers used an emission inventory compiled in 1974 which,

when converted from a mass basis to a volume basis, suggested a spatially-averaged VOC/NO_x ratio of 4.7. This is comparable to the VOC/NO_x emission ratio of 5:1 that was used to generate the basecase ozone profile shown in Figure 9.

Using the emission-driven scenario, Tesche et al. (1984) compared the effect of reducing VOC emissions by 50% versus the effect of reducing both VOC and NO_x emissions by 50%. They found that reductions in VOC alone led to a 25% decrease in the basinwide O_3 maximum. When both VOC and NO_x were reduced, the basinwide O_3 maximum was decreased by only 20%. In contrast to the earlier study, Tesche et al. concluded that NO_x control accompanied by VOC control is less effective than control of VOC emissions alone. This finding is in agreement with the results presented in Figure 9.

Both the box model used in this study and the urban airshed modeling results suggest that control of both VOC and NO_x could be more effective in lowering daily maximum O_3 levels than control of VOC alone if the simulations are governed by VOC/NO_x ratios derived from ambient measurements. The reverse appears to be true if the simulations are driven by ozone-precursor ratios that are derived from emission inventories.

CONCLUSIONS

The results presented in this paper, as well as the results obtained in other modeling studies, leave little doubt that VOC reduction is the most effective strategy for reducing ozone levels in urban areas having VOC/NO_x ratios of 10 or less. At VOC/NO_x ratios of 20 or more, NO_x reduction is clearly the most effective strategy for reducing ozone. At intermediate ratios between approximately 10:1 and 20:1, control of either VOC or NO_x could be an effective strategy for reducing ozone levels. Which one will be the most effective will

depend on a number of factors. For urban areas having typical VOC/NO_x ratios (<15:1), VOC control will probably be the most effective strategy for achieving the ozone standard. At higher ratios (>15:1), NO_x reduction may be more effective for achieving the ozone standard. The results obtained in this study, however, suggest that NO_x control can lead to an increase in ozone levels near source areas; consequently, a greater fraction of the population may be exposed to high ozone levels if such a strategy is adopted.

The profiles presented in Figures 6-9 demonstrate that the critical factor in determining the most effective control measure for reducing urban O_3 levels is the VOC/NO_x ratio. Depending on the assumptions made regarding the ratio of the O_3-precursor emissions, a strategy involving simultaneous reduction of VOC and NO_x may be more or less effective in reducing downwind ozone levels than a strategy involving reduction of only VOC. Given the present uncertainty in emission inventories, it is difficult to assess which control strategy would be the most effective.

In order to judge the effectiveness of simultaneous VOC and NO_x control, the accuracy of existing emission data bases needs to be determined. A more complete and accurate data base of ambient VOC/NO_x ratios in urban areas also should be acquired. Until emissions and ambient measurements are reconciled, we should be very cautious about embarking on any control program that involves reductions in NO_x. Such a strategy could have a detrimental impact on urban ozone levels.

REFERENCES

Baugues, K. A. (1986) "A Review of NMOC, NO_x and NMOC/NO_x Ratios Measured in 1984 and 1985," U.S. Environmental Protection Agency Report EPA-450/4-86-015, Research Triangle Park, NC.

Baugues, K. A. (1987) "Support Document for Selection of Default Upper Air Parameters," In preparation, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Monitoring and Data Analysis Division, Research Triangle Park, NC.

California Air Resources Board (1986) Technical Support Division, "The Effects of Oxides of Nitrogen on California Air Quality, Report # TSD-85-01.

Ching, J. K. S., Novak, J. H., Schere, K. L., and Schiermeier, F. A. (1986) "Reconciliation of Urban Emissions and Corresponding Ambient Air Concentrations Using Mass Flow Rate Technique," Internal Document, U. S. Environmental Protection Agency, Atmospheric Sciences Research Laboratory, Research Triangle Park, NC.

Gipson, G. L. (1984a) "User's Manual for OZIPM-2: Ozone Isopleth Plotting with Optional Mechanisms/Version 2," U.S. Environmental Protection Agency Report EPA-450/4-84-024, Research Triangle Park, NC.

Gipson, G. L. (1984b) "Sensitivity of EKMA/CB-3 to Organic Reactivity," Internal Document, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Monitoring and Data Analysis Division, Research Triangle Park, NC.

Jeffries, H. E. (1987) "User's Guide to Photochemical Kinetics Simulation System," Internal Document, University of North Carolina, School of Public Health, Chapel Hill, NC.

Meyer, E. L. (1986) "Review of Control Strategies for Ozone and Their Effects on Other Environmental Issues," U.S. Environmental Protection Agency Report EPA-450/4-86-011, Research Triangle Park, NC.

South Coast Air Quality Management District (1981) "Review of SAI Airshed Model Sensitivity Study Conducted for the South Coast Air Basin by California Air Resources Board," AQMP Technical Paper No. 5.

Tesche, T. W., Seigneur, C., Oliver, W. R., and Haney, J. L. (1984) "Modeling Ozone Control Strategies in Los Angeles," J. Environ. Eng., 110, 208-225.

Westberg, H. and Lamb, B. (1985) "Ozone Production and Transport in the Atlanta, Georgia Region," U.S. Environmental Protection Agency Report EPA/600/3-85/013

Whitten, G. Z. and Gery, M. W. (1986) "Development of CBM-X Mechanisms for Urban and Regional AQSMs," U.S. Environmental Protection Agency

Report EPA/600/3-86/012, Research Triangle Park, NC.

U.S. Environmental Protection Agency (1977) "Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors," EPA-450/2-77-021a, Research Triangle Park, NC.

U. S. Environmental Protection Agency (1982) "Air Quality Criteria for Oxides of Nitrogen," EPA-600/8-82-0-26, pages 5-13, Research Triangle Park, NC.

FIGURE 1

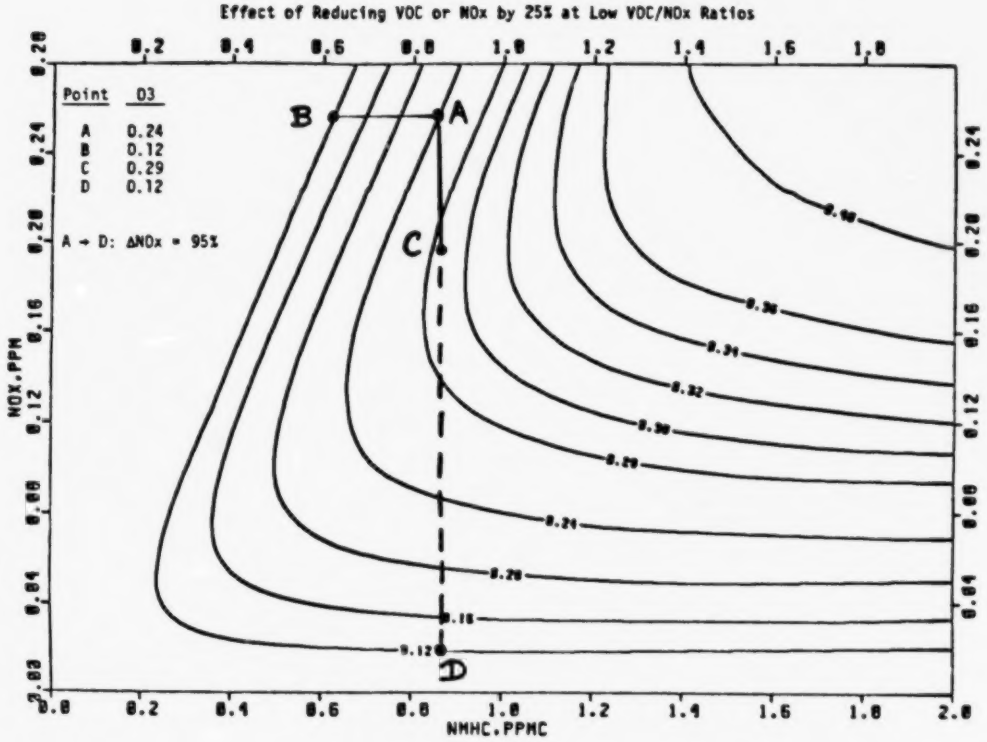


FIGURE 2

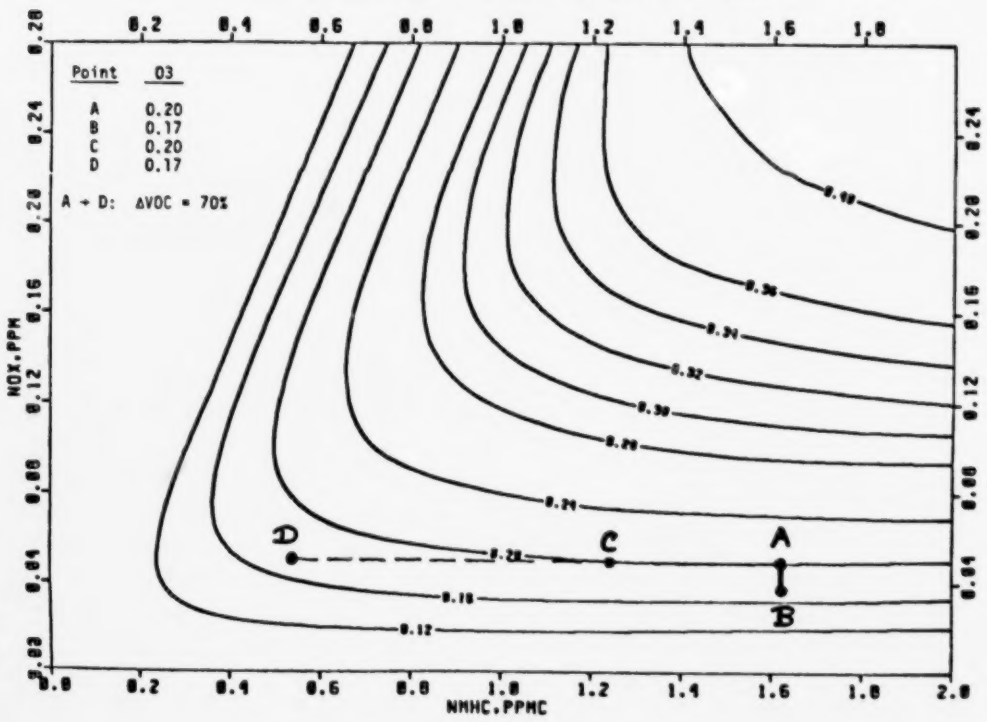


FIGURE 3

Effect of Reducing VOC and NOx by 25% at Intermediate VOC/NOx Ratios

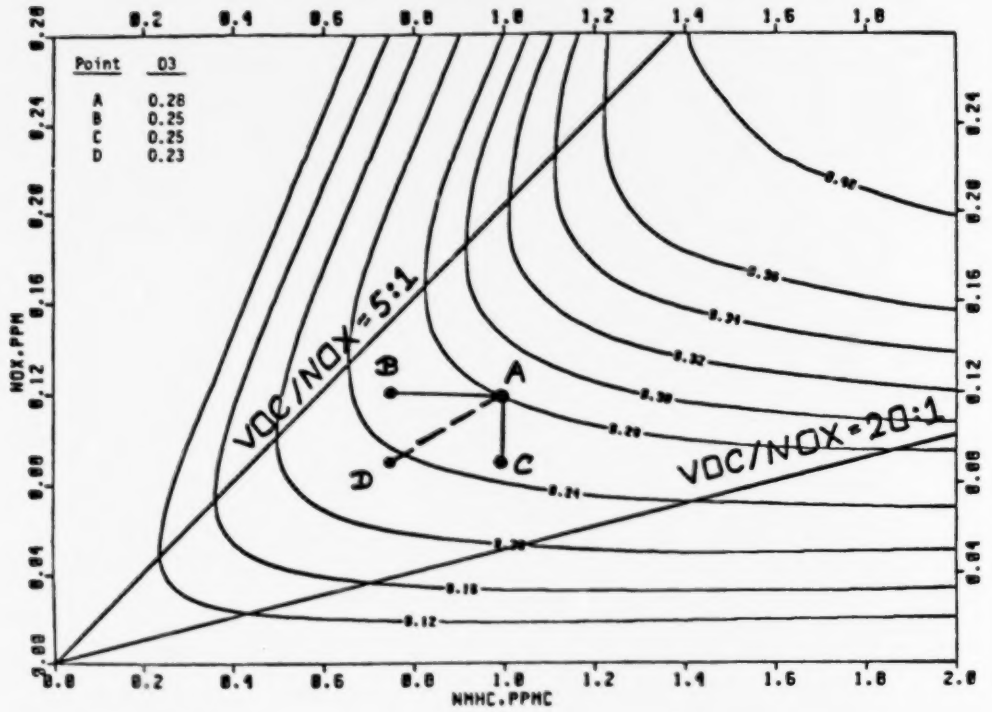


FIGURE 4

Control Measures Needed to Achieve Ozone Standard at VOC/NOx = 12:1

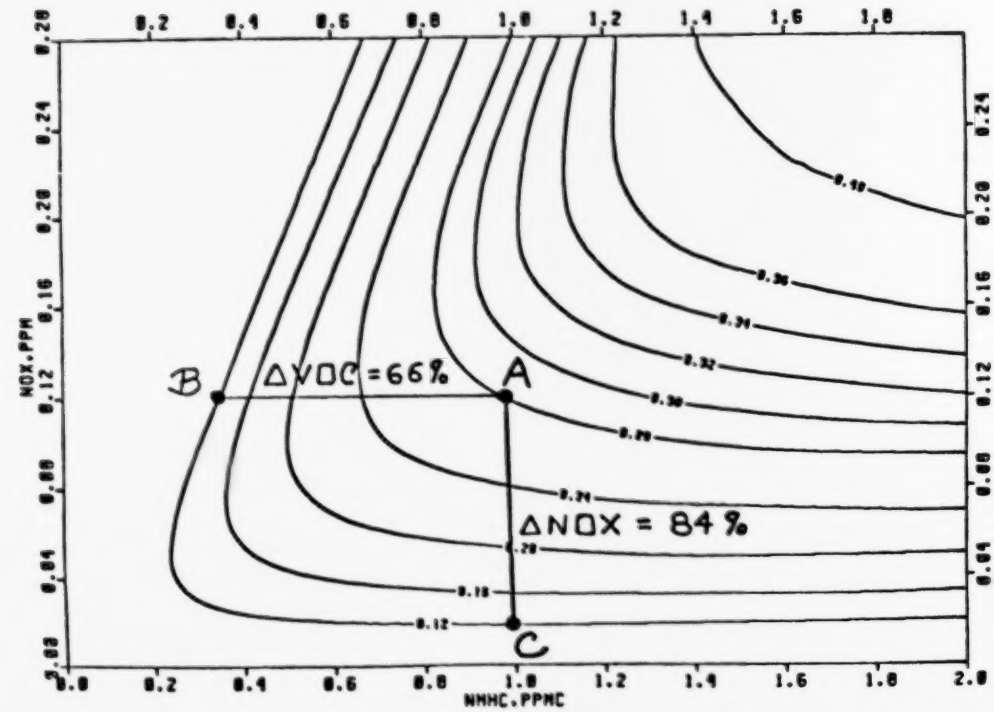
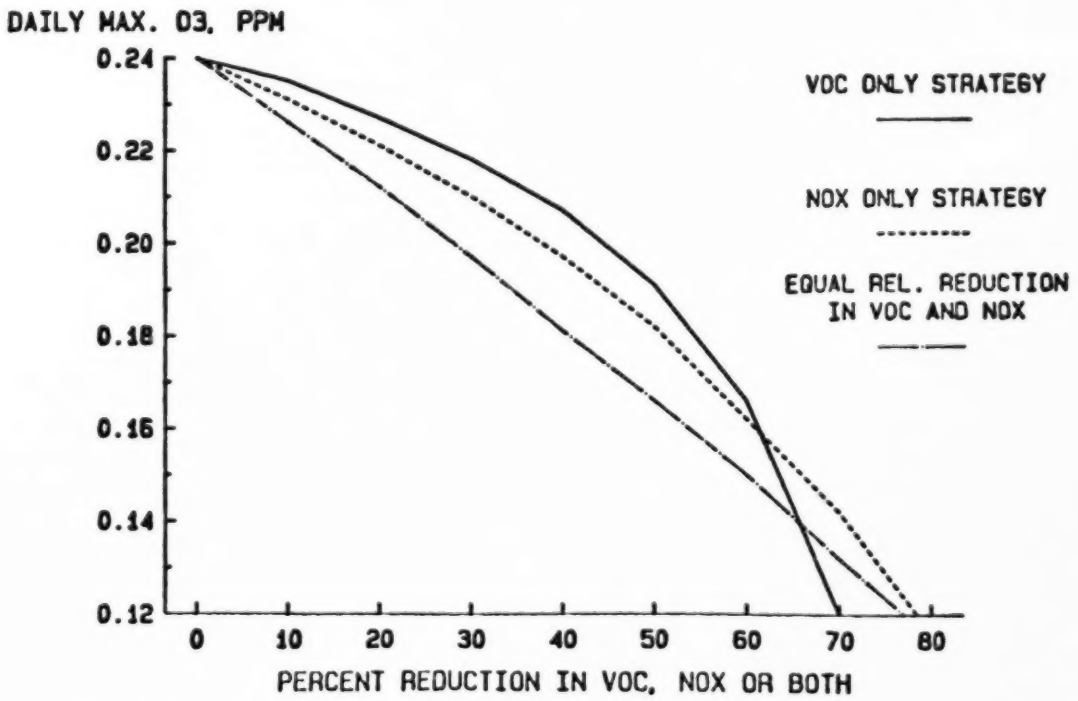


FIGURE 5

DAILY MAXIMUM OZONE AS A FUNCTION OF APPLIED CONTROLS



VOC/NOX RATIO = 12:1

SOURCE: MEYER (1986)

FIGURE 6

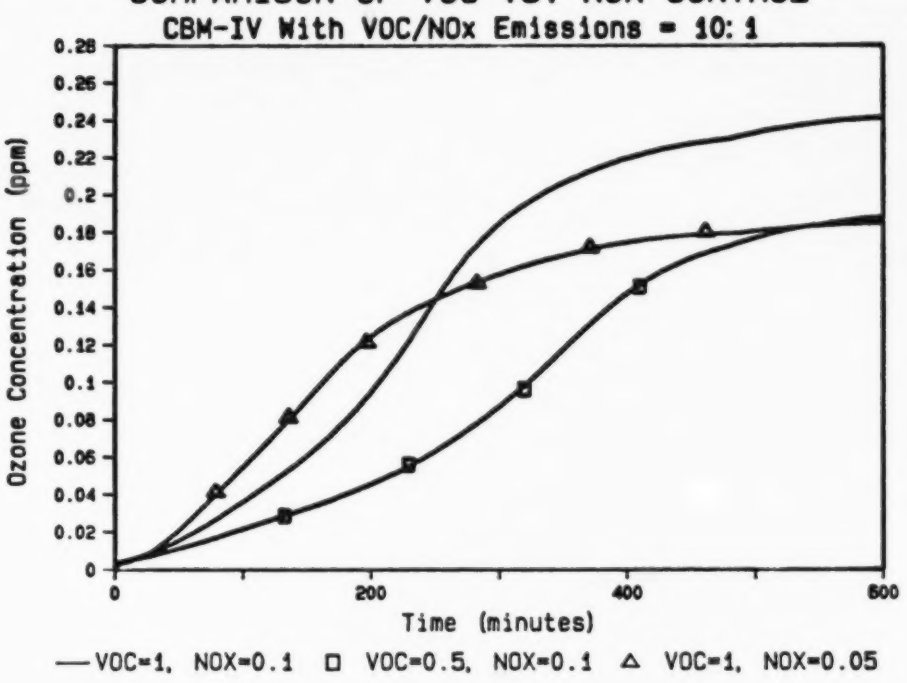


FIGURE 7

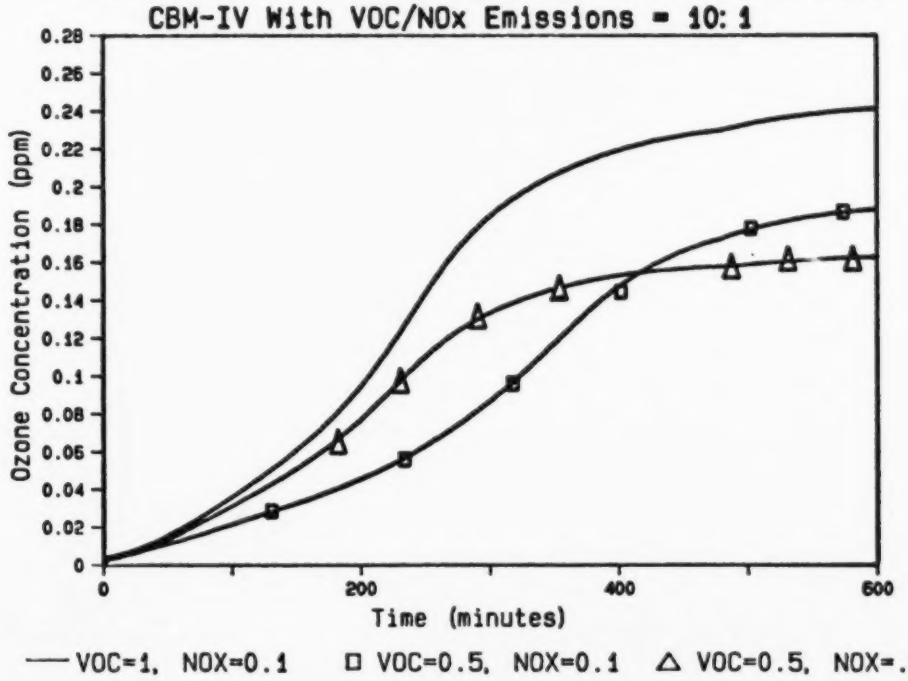
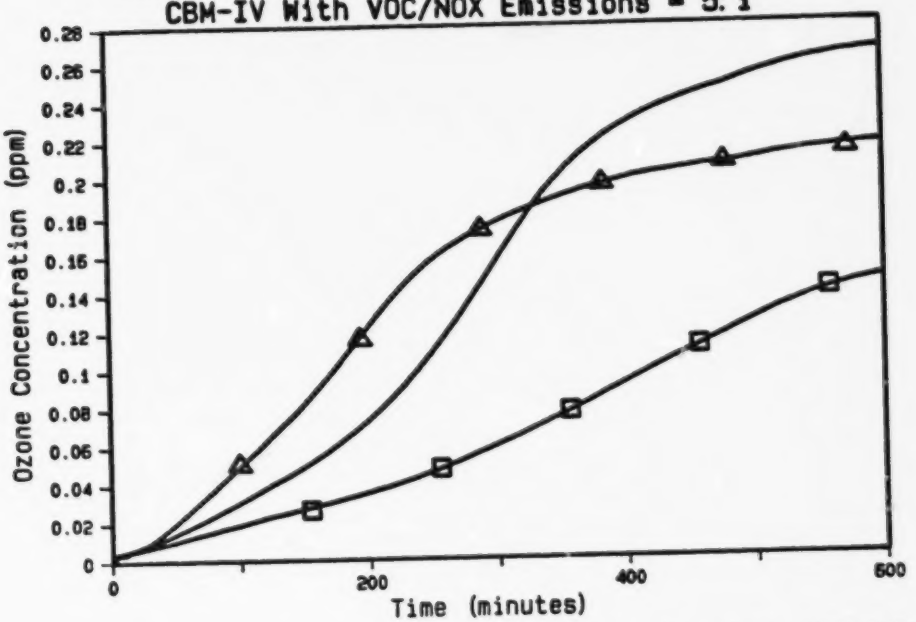


FIGURE 8

COMPARISON OF VOC VS. NOX CONTROL

CBM-IV With VOC/NOX Emissions = 5: 1

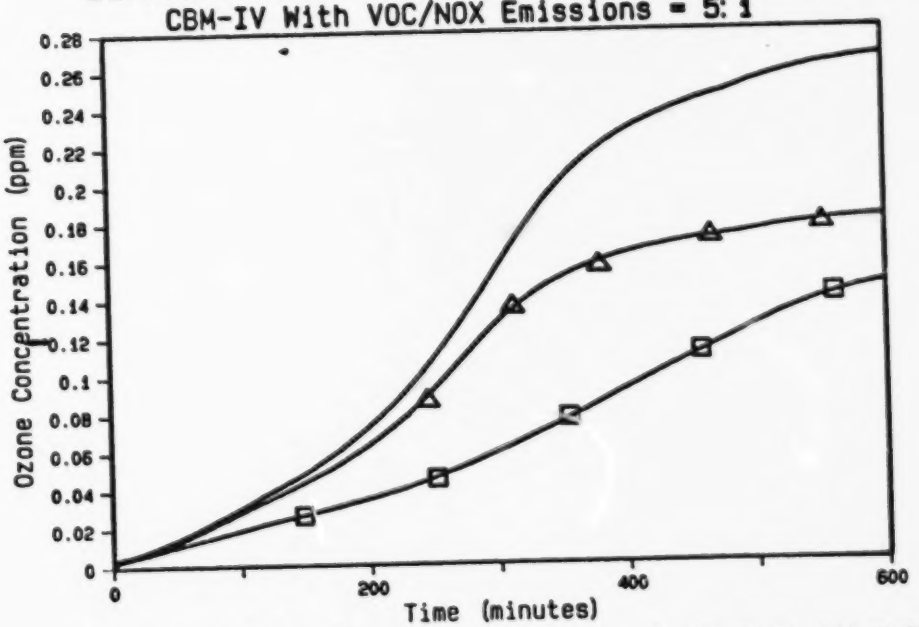


— VOC=1, NOX=0.1 □ VOC=0.5, NOX=0.1 △ VOC=1, NOX=0.05

FIGURE 9

COMPARISON OF VOC VS. VOC + NOX CONTROL

CBM-IV With VOC/NOX Emissions = 5: 1



— VOC=1, NOX=0.1 □ VOC=0.5, NOX=0.1 △ VOC=0.5, NOX=0.05